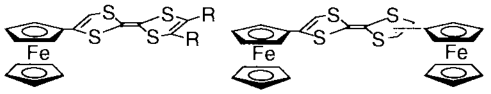
Synthesis and Properties of Tetrathiafulvalene-Substituted Ferrocenes

Masahiko Iyoda,* Takahiro Takano, Naoki Otani, Kohei Ugawa, Masato Yoshida, Haruo Matsuyama,
and Yoshiyuki Kuwatani
Department of Chemistry, Graduate School of Science, Tokyo Metropolitan University, Hachioji, Tokyo 192-0397

(Received September 10, 2001; CL-010884)

1-Tetrathiafulvalenylferrocene and its derivatives have been synthesized in moderate to good yields employing palladium-catalyzed cross-coupling. The oxidation potentials of the title compounds revealed enhanced donor ability of the TTF unit, whereas the donor ability of the ferrocene moiety decreased markedly. The radical-cation salts derived from 1-tetrathiafulvalenylferrocenes are semiconductors.

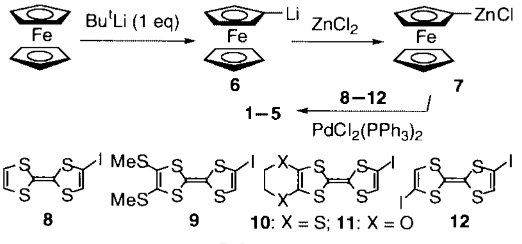
TTF (tetrathiafulvalene) is known as a π-donor molecule, and its CT-complex with TCNQ (tetracyanoquinodimethane) shows high electric conductivity.[1] Ferrocene is a famous organometallic sandwich complex with donor properties,[2] and the CT-complex of decamethylferrocene with TCNE (tetracyanoethylene) shows ferromagnetic properties.[3] Thus, a donor system containing both TTF and ferrocene units can be expected to behave like a bicephalous donor.[4]



1: R = H
2: R = SMe
3: R, R = SCH_2CH_2S
4: R, R = OCH_2CH_2O

5a: trans **5b**: cis

Syntheses of **1**–**5** were carried out using the palladium-catalyzed cross-coupling reaction as shown in Scheme 1. Ferrocene was treated with Bu^tLi (1.0 equiv) in THF at –78 °C to form 1-lithioferrocene **6** which was converted into ferrocenylzinc chloride **7** by treatment with zinc chloride in THF.[5] The cross-coupling reaction of **7** with iodo-TTF **8** in the presence of $PdCl_2(PPh_3)_2$ (10 mol%) proceeded smoothly to afford **1** in 81% yield.[6] Similarly, the reaction of **7** with BMT-TTFI **9**, EDT-TTFI **10**, and EDO-TTFI **11** in the presence of $PdCl_2(PPh_3)_2$ (10 mol%) produced the corresponding TTF-ferrocenes **2**, **3**, and **4** in 82, 84, and 77% yields, respectively. In the case of **5**, the reaction of **7** (5 equiv) with diiodo-TTF **12** in the presence of $PdCl_2(PPh_3)_2$ (10 mol%) afforded **5** in 67% yield. Although a mixture of cis- and trans-isomers of **5** was synthesized using another procedure,[7] pure *trans*-**5** can be prepared in a better yield using our method reported here.



Scheme 1.

The oxidation potentials of **1**–**5**, TTF, and ferrocene measured by cyclic voltammetry are shown in Table 1. The TTF-ferrocenes (**1**–**5**) show three reversible redox waves corresponding to oxidation of TTF and ferrocene. It is worth noting that the first oxidation potentials (TTF → $TTF^{+\bullet}$) of **1** and **5** are slightly smaller than that of TTF, reflecting enhanced donor ability of the TTF moieties. Since ferrocene can stabilize the neighboring carbocation, the TTF cation-radicals may be stabilized by the ferrocene moiety in **1** and **5**. On the contrary, the second oxidation potentials (Fc → Fc^+) in **1**–**5** decreased substantially as compared to the oxidation potential of ferrocene, presumably due to the effect of the neighboring cations. The third oxidation potentials ($TTF^{+\bullet}$ → TTF^{2+}) in **1**–**5** are also more positive than that of TTF, reflecting larger interaction between the cations.

Table 1. Oxidation potentials measured by cyclic voltammetry[a]

	$E^1_{1/2}$	$E^2_{1/2}$	$E^3_{1/2}$
Fc	+0.46		
TTF	+0.37	+0.74	
1	+0.35	+0.71	+0.85
2	+0.40	+0.68	+0.82
3	+0.41	+0.70	+0.86
4	+0.37	+0.69	+0.84
5a	+0.33	+0.69 (2e)	+0.92

[a] V vs SCE, 0.1M Bu_4NClO_4 in PhCN.

The structure of **1** was determined by X-ray analysis.[8] The TTF and ferrocene subunits in **1** possess their own structural feature, and the two donor molecules in **1** are connected with coplanarity of the cyclopentadienide ring and the tetrathiafulvalene unit. As expected from the oxidation potentials, **1**–**5** form CT-complexes with TCNQ, DDQ, and $TCNQF_4$.[8] However, electric conductivity of these CT-complexes proved to be very low like that of an insulator.

For preparation of the cation radical salts, **1**–**5** were oxidized in an electrocrystallization cell in the presence of $Bu^n_4N^+X^-$ by controlled electrolysis at constant current. In the case of I_3^- and $M(dmit)_2^-$ salts (H_2dmit = 4,5-dimercapo-1,3-dithiole-2-thione), **1**–**5** were directly oxidized by mixing a solution of **1**–**5** with a solution of iodine. Although the cation radical salts of **1**–**5** with ClO_4^-, PF_6^-, BF_4^-, AuI_3^-, I_3^-, IBr_2^-, and I_2Br^- as the counter anions were insulators, the salts of **1**–**5** with $M(dmit)_2^-$ (M = Ni, Pd, and Pt) were semi-conductors (Table 2).

Slow mixing of a solution of **1** and $Ni(dmit)_2{\cdot}(Bu^n_4N)_2$ in CH_2Cl_2 with a solution of I_2 in CH_2Cl_2 formed single crystals. The structure of **1**·$Ni(dmit)_2$ was determined by X-ray analysis.[9] As shown in Figure 1, the TTF moiety in **1** and $Ni(dmit)_2$ stack face-to-face (3.34 Å). The cyclopentadienide ring and the TTF unit show coplanarity with a torsion angle of 9.5°. The central C–C bond distance of the TTF unit is 1.384(9) Å which is

Table 2. Electric conductivities of **1**–**5a**·M(dmit)$_2$[a]

	M = Ni	M = Pd	M = Pt
1	6.4×10^{-6} [c]		1.7×10^{-7} [c]
2	1.7×10^{-5} [c]		
3	2.6×10^{-7} [b]	6.0×10^{-7} [b]	4.2×10^{-6} [c]
4	1.6×10^{-5} [c]		2.1×10^{-5} [c]
5a	2.6×10^{-5} [b]	2.1×10^{-5} [c]	

[a] Room-temperature conductivity measured by a two-probe technique. [b] Measured on a single crystal. [c] Measured on a compressed pellet.

longer than that (1.35 Å) of the neutral TTF, whereas the average C–Fe distance in the ferrocene moiety is 2.04 Å similar to that of the neutral ferrocene. In addition, an edge of the TTF ring and a double bond in Ni(dmit)$_2$ are located closely with distances of 3.5–3.6 Å. Since TTF$^{+\bullet}$ and Ni(dmit)$_2^{-\bullet}$ form a mixed-stacking column, dimeric Ni(dmit)$_2^{-\bullet}$ may contribute to show electric conductivity of **1**·Ni(dmit)$_2$ using a side-by-side interaction.

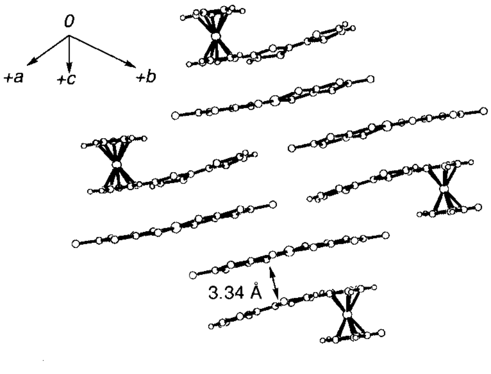


Figure 1. Crystal structure of **1**·Ni(dmit)$_2$.

In order to examine the intramolecular interaction between the TTF and ferrocene moieties in solution, the electronic spectra of the cationic species $\mathbf{3}^{+\bullet}$, $\mathbf{3}^{2+}$, and $\mathbf{3}^{3+}$ derived from **3** with 1, 3 and 5 equivs of Fe(ClO$_4$)$_3$, respectively, were measured in CH$_3$CN. Since the electronic spectra of $\mathbf{3}^{+\bullet}$, $\mathbf{3}^{2+}$, and $\mathbf{3}^{3+}$ were measured in very diluted solutions over the concentration range of 6.5×10^{-5} to 2.0×10^{-4}, intermolecular π–π stacking of these cationic species can be ruled out.[10] As shown in Table 3, the electronic spectrum of $\mathbf{3}^{+\bullet}$ shows an intense absorption at 748 nm with a broad absorption at 1172 nm. The peak at 748 nm is assigned to the absorption of the TTF cation radical, and that at 1172 nm may be assigned to the CT-band based on the TTF cation radical to the neutral ferrocene. In contrast, the spectrum of $\mathbf{3}^{2+}$ consists of the absorption band of TTF cation radical without charge-transfer interaction. The spectrum of $\mathbf{3}^{3+}$ corresponds to that of TTF^{2+}. The longest absorption maxima of the ferrocenium part in $\mathbf{3}^{2+}$ and $\mathbf{3}^{3+}$ may be concealed by the strong absorption of the TTF cation radical and dication.

Table 3. Electonic spectra of **3**, $\mathbf{3}^{+\bullet}$, $\mathbf{3}^{2+}$, and $\mathbf{3}^{3+}$ in CH$_3$CN[a]

	λ_{max} nm (log ε)[b]
3	314 (4.05)
$\mathbf{3}^{+\bullet}$	452 (3.95), 748 (3.82), 1172 br (3.28)
$\mathbf{3}^{2+}$	440 (3.80), 754 (3.38)
$\mathbf{3}^{3+}$	652 (4.03)

[a] **3** oxidized by Fe(ClO$_4$)$_3$ in CH$_3$CN. Concentration: **3**, 3.9×10^{-4} M; $\mathbf{3}^{+\bullet}$, 2.0×10^{-4} M; $\mathbf{3}^{2+}$, 9.8×10^{-5} M; $\mathbf{3}^{3+}$, 6.5×10^{-5} M. [b] log ε calculated by assuming a quantitative conversion of **3** to the corresponding cationic species.

We have disclosed a novel electronic interaction of the TTF- and ferrocene-moieties in the neutral and cationic states. The cation radicals derived from **1**–**5** show ESR signals (g = *ca.* 2.011). However, the instability of the corresponding dications precludes study of the spin–spin interaction between the TTF$^{+\bullet}$ and ferrocenium ions in **1**–**5**. Further studies on the properties of TTF$^{+\bullet}$ and Fc^{+} ions are now in progress.

References and Notes

1 For general reviews, see a) D. J. Sandman and G. P. Ceasar, *Isr. J. Chem.*, **27**, 293 (1986). b) M. R. Bryce, *Aldchimica Acta*, **18**, 73 (1985). c) M. R. Bryce and L. C. Murphy, *Nature*, **309**, 119 (1984). d) J. H. Perlstein, *Angew. Chem., Int. Ed. Engl.*, **16**, 519 (1977).

2 C. L. Vanda, K. Bechgaard, D. O. Cowan, U. T. Mueller-Westerhoff, P. Eilbracht, G. A. Candela, and R. L. Collins, *J. Am. Chem. Soc.*, **98**, 3181 (1976); J. A. Kramer and D. N. Hendrickson, *Inorg. Chem.*, **19**, 3330 (1980); T.-Y. Dong, D. N. Hendrickson, K. Iwai, M. J. Cohn, S. J. Geib, A. L. Rheingold, H. Sano, I. Motoyama, and S. Nakashima, *J. Am. Chem. Soc.*, **107**, 7996 (1985); S. Barlow, V. J. Murphy, J. S. O. Evans, and D. O'Hare, *Organometallics*, **14**, 3461 (1995).

3 J. S. Miller and A. J. Epstein, *Angew. Chem., Int. Ed. Engl.*, **33**, 385 (1994).

4 a) H.-J. Lee, D.-Y. Noh, A. E. Underhill, and C.-S. Lee, *J. Mater. Chem.*, **9**, 2359 (1999). b) S. B. Wilkes, I. R. Butler, A. E. Underhill, M. B. Hursthouse, D. E. Hibbs, and K. M. A. Malik, *J. Chem. Soc., Dalton Trans.*, **1995**, 897. c) A. S. Moore, P. J. Skabara, M. R. Bryce, A. S. Batsanov, J. A. K. Howard, and S. T. A. K. Daley, *J. Chem. Soc., Chem. Commun.*, **1993**, 417.

5 M. Iyoda, T. Okabe, T. Kondo, S. Sasaki, H. Matsuyama, Y. Kuwatani, and M. Katada, *Chem. Lett.*, **1997**, 103, and references cited therein.

6 All new compounds gave satisfactory spectral data. **1**: orange crystals, mp 195.0–196.0 °C (decomp.); EIMS *m/z* 388 (M$^+$); ^{1}H NMR (CDCl$_3$) δ 4.222 (s, 5H), 4.262 (t, *J* = 1.8 Hz, 2H), 4.398 (t, *J* = 1.8, 2H), 6.108 (s, 1H), 6.333 (s, 2H); ^{13}C NMR (CDCl$_3$) δ 67.06, 69.02, 69.83, 78.27, 100.56, 109.46, 119.06, 119.10, 134.93. Found: M$^+$ 387.9187. Calcd for C$_{16}$H$_{12}$S$_4$Fe: MW 387.9171. **2**: dark red crystals, mp 126.5–127.2 °C; EIMS *m/z* 480 (M$^+$); ^{1}H NMR (CDCl$_3$) δ 2.347 (s, 3H), 2.459 (s, 3H), 4.219 (s, 5H), 4.269 (t, *J* = 1.2 Hz, 2H), 4.393 (t, *J* = 1.2, 2H), 6.111 (s, 1H); ^{13}C NMR (CDCl$_3$) δ 19.20, 67.07, 69.07, 69.80, 78.17, 108.97, 115.40, 127.51, 127.57, 134.89. Found: M$^+$ 479.8911. Calcd for C$_{18}$H$_{16}$S$_6$Fe: MW 479.8926. **3**: red needles, mp 118.7–119.5 °C; EIMS *m/z* 478 (M$^+$); ^{1}H NMR (CDCl$_3$) δ 3.305 (s, 4H), 4.214 (s, 5H), 4.267 (t, *J* = 1.9 Hz, 2H), 4.392 (t, *J* = 1.9, 2H), 6.100 (s, 1H); ^{13}C NMR (CDCl$_3$) δ 30.40, 67.05, 69.15, 69.89, 78.03, 109.05, 113.72, 113.78, 117.77, 134.74. Found: M$^+$ 477.8778. Calcd for C$_{18}$H$_{14}$S$_6$Fe: MW 477.8770. **4**: red crystals, mp 174.0–175.0 °C (decomp.); EIMS *m/z* 446 (M$^+$); ^{1}H NMR (CDCl$_3$) δ 4.213 (s, 5H), 4.264 (s, 4H) 4.271 (t, *J* = 1.6 Hz, 2H), 4.393 (t, *J* = 1.6, 2H), 6.114 (s, 1H); ^{13}C NMR (CDCl$_3$) δ 66.24, 67.06, 69.07, 69.84, 78.23, 108.96, 116.06, 123.20, 123.25, 134.92. Found: M$^+$ 445.9238. Calcd for C$_{18}$H$_{14}$O$_2$S$_4$Fe: MW 445.9226. **5a**: orange plates, mp 158.3–158.9 °C; EIMS *m/z* 572 (M$^+$); ^{1}H NMR (CDCl$_3$) δ 4.109 (s, 10H), 4.173 (t, *J* = 1.8 Hz, 4H), 4.306 (t, *J* = 1.8, 4H), 6.101 (s, 2H); ^{13}C NMR (CDCl$_3$) δ 67.02, 69.07, 69.97, 78.29, 100.25, 109.36, 133.73. Found: M$^+$ 571.9129. Calcd for C$_{26}$H$_{20}$S$_4$Fe$_2$: MW 571.9147.

7 Y. Ueno, H. Sano, and M. Okawara, *J. Chem. Soc., Chem. Commun.*, **1980**, 28.

8 The X-ray analysis of **1**, **3**, **5a**, and **3**·TCNQ will be reported in a full paper.

9 **1**·Ni(dmit)$_2$: C$_{22}$H$_{12}$S$_{14}$FeNi, MW 839.72, triclinic, space group $P\bar{1}$ (No. 2), a = 11.291(3), b = 15.938(7), c = 8.564(3) Å, α = 98.08(3)°, β = 105.81(3)°, γ = 85.11(3)°, V = 1466.3(10) Å^3, Z = 2, D_c = 1.902 g cm^{-3}, R_1 = 0.057, R_w = 0.091.

10 K. Lahlil, A. Moradpour, C. Bowlas, F. Menou, P. Cassoux, J. Bonvoisin, J.-P. Launay, G. Dive, and D. Dehareng, *J. Am. Chem. Soc.* **117**, 9995 (1995).